TITLE: AN INNOVATIVE CONCEPT FOR CO_2-BASED TRI GENERATION OF FUELS, CHEMICALS, AND ELECTRICITY USING FLUE GAS IN VISION 21-PLANT

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ABSTRACT

OBJECTIVE

The objective of this UCR Innovative Concept project is to explore the feasibility of the concept of CO_2-based tri-generation of fuels, electricity, and chemicals via tri-reforming using flue gas from power plants without CO_2 separation. As a key component in the proposed concept, tri-reforming of natural gas using CO_2, steam, and O_2 in the flue gas without CO_2 separation will be investigated by both computational and experimental approaches. Computational thermodynamic analysis is used to obtain the equilibrium conversion and product distribution such as H_2/CO ratio as well as equilibrium energy requirements and equilibrium carbon formation in the tri-reforming system. The experimental study is to

verify the tri-reforming process producing syngas with desired H_2/CO ratio under certain process conditions and reactant gas compositions. The tested catalysts in this project will be selected from current industrial Ni-based steam reforming catalysts. The kinetic carbon formation in tri-reforming system will also be studied.

ACCOMPLISHEMENTS TO DATE

The thermodynamic analysis of tri-reforming was performed based on the gas compositions simulating flue gas from coal-fired and gas-fired power plants. The analysis included the effect of steam/CO_2 in reactants on H_2/CO ratio in the product, the effect of temperatures on methane conversion, and the effect of O_2 on methane conversion and system energy requirement. The calculation results indicate that steam/CO_2 in reactants is an important factor to determine the H_2/CO in the product. More O_2 present in the reactant can reduce the energy requirement for the whole system and increase methane conversion, but reduce the CO_2 conversion as well. In the combined steam-CO_2 reforming and tri-reforming, carbon formation is less thermodynamically favored compared to that from CO_2 reforming.

The tri-reforming experiments were conducted at 850…C at 1 atm using a fixed-bed reactor where about 100 mg of catalyst sample (Haldor-Topsoe R67 Ni-based catalyst) was placed. Different compositions of gases including CH_4+CO_2 (1:1 mole ratio), CH_4+CO_2+O_2 (1:1:0.1), CH_4+H_2O (1:1), CH_4+H_2O (1:1), CH_4+H_2O+O_2 (1:1:0.1), CH_4+CO_2+H_2O+O_2 (1:1:1:0.1), and CH_4+CO_2+H_2O+O_2 (1:1:2:0.1) were tested as feed for the tri-reforming reaction. The results showed that CO_2 reforming alone gave high CO_2 and CH_4 conversion but lower H_2/CO ratio (< 1) and was accompanied by significant coke formation. Steam reforming gave higher CH_4 conversion but higher H_2/CO ratios (≥ 3). Addition of O_2 into steam reforming and CO_2 reforming did not change their product H_2/CO significantly. However, combined CO_2-steam reforming and tri-reforming produced syngas with H_2/CO ratios close to 2. When steam/CO_2 in the feed was 2, the desirable syngas for methanol synthesis and F-T synthesis with H_2/CO ratio of 2 was obtained by a single tri-reforming reaction. Moreover, unlike CO_2 reforming, the tri-reforming did not show any observable decrease of activity due to coke formation under the reaction conditions. These results are in good agreement with the computational results.

Kinetic carbon formation during combined and tri-reforming was also studied. The study was carried out using an unique Tapered Element Oscillating Microbalance (TEOM). The TEOM microbalance is capable of measuring mass change accurately at real reaction conditions (high temperatures and pressures) while avoiding by-pass and buoyancy effect in a traditional gravimetric microbalance. Kinetic carbon formation in CO_2 reforming and steam reforming has been measured at 650…C~ 700…C at atmospheric pressure over Haldor Topsoe R67 and ICI R15513 catalysts. Since CO_2 reforming showed severe carbon formation problem, O_2 was introduced into the CO_2 reforming system to investigate the effect of O_2 on carbon formation rate. The results showed that introduction of small amount of O_2 significantly reduced carbon formation rate while, at the same time, increased methane conversion and H_2 and CO yields. It was also observed from our experiments that reactions consuming O_2 were faster and took place at the inlet of reactor, which indicates further design of catalysts tailored for tri-reforming reaction is necessary.

Several laboratory prepared Pt-based catalysts with different promoters have been tested in tri-reforming reaction. The preliminary results indicated Pt catalyst promoted by Vanadium gave the highest activity and selectivity for CO2 conversion to CO in the presence of O_2. Further work is in progress.

FUTURE WORK

Our present computational and experimental study has shown the feasibility of the proposed concept. Future work will include the optimization of operation conditions using simulated and real flue gas from power plants as feed and modification of fixed-bed reactor in order to fit the requirement for high throughput reforming. Development of new catalysts tailored for tri-reforming reaction will be considered in future work.

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